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compared with an aqueous electrolyte, is used as the electrolyte, electrolysis is likely to take place due to impurities, particularly water, contained in the electrolyte. Accordingly, for the organic electrolyte, both the solvent and the electrolytic salt will be used as highly purified and dehydrated.

On the other hand, for the electrodes for an electric double layer capacitor, an electrode material having a high surface area is used, and when it is to be combined with the above organic electrolyte, activated carbon is usually employed as the electrode material having a high surface area. Activated carbon is a porous material having fine pores of a few nm, but it is likely to adsorb moisture in the environment, as it has a high adsorbing ability. Accordingly, activated carbon is required to be highly dehydrated during the process for producing an electric double layer capacitor.

In order to completely remove moisture from fine pores of activated carbon, it is usually required to carry out dehydration treatment at a high temperature of at least 300°C in vacuum or in an inert gas atmosphere. However, activated carbon particles are usually molded by means of a binder such as an organic polymer on a current collector to form an electrode, and the binder undergoes thermal decomposition by high temperature treatment of at least 300°C. Therefore, heat treatment may usually be

possible only at a temperature of not higher than 200°C, whereby it is difficult to completely remove moisture in the activated carbon electrode.

For the purpose of increasing the energy density, an electric double layer capacitor employing an organic electrolyte is operated at a voltage of at least 2 V which is higher than the theoretical decomposition voltage (1.23 V) of water. Therefore, when a capacitor cell is assembled and then a voltage is applied for operation, moisture remaining in the pores will be electrolyzed to generate a gas. It has been found that the generated gas will gradually accumulate in pores of activated carbon and will remain in the interior of the element comprising electrodes facing each other with a separator interposed between them and impregnated with the electrolyte, without being discharged from the element.

If the capacitor is used for a long period of time under such a condition, the electrolyte in pores will be expelled by the generated gas, whereby the expected capacitance will not be obtained. Further, electrically conductive paths by ion transfer within pores will be cut off, thus leading to deterioration of the performance such as a decrease in the capacitance or an increase of the internal resistance.

Under these circumstances, it is an object of the

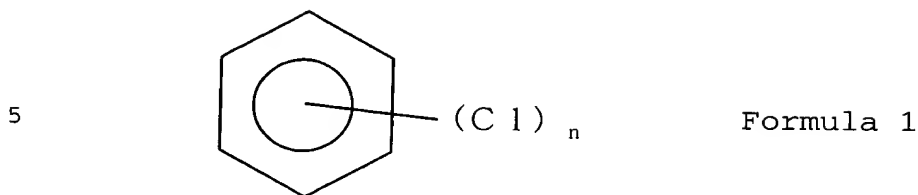
present invention to solve the above-mentioned problems of the prior art and to provide a method for producing an electric double layer capacitor which is excellent in reliability of the performance for a long period of time and which has a high operation voltage and a high energy density.

The present invention provides a method for producing an electric double layer capacitor, which comprises impregnating an element comprising positive and negative electrodes facing each other with a separator interposed between them, with an organic electrolyte capable of forming an electric double layer on the surface of the electrodes to store electric charge, and then applying a voltage to the element, wherein said positive and negative electrodes are made of electrodes containing a carbonaceous material having a specific surface area of from 100 to 3,000 m²/g, and said organic electrolyte contains benzene or its chlorine derivative having at least one hydrogen atom of benzene substituted by a chlorine atom.

Now, the present invention will be described in detail with reference to the preferred embodiments.

In the present invention, benzene or its chlorine derivative having at least one hydrogen atom of benzene substituted by a chlorine atom (hereinafter referred to as "a chlorine derivative of benzene") is represented by

a compound of the formula 1. In the formula 1, n is an integer of from 1 to 6.



In the present invention, the benzene or its chlorine derivative is preferably at least one member selected from the group consisting of benzene, monochlorobenzene, dichlorobenzene and trichlorobenzene. The structure of dichlorobenzene is not particularly limited, and any one of o-dichlorobenzene, m-dichlorobenzene and p-dichlorobenzene may be preferably employed. Likewise, the structure of trichlorobenzene is not particularly limited.

In the present invention, the amount of the benzene or its chlorine derivative in the electrolyte may suitably be adjusted depending upon the amount of the remaining moisture or the pore characteristics of the carbonaceous material contained in the electrodes. It is preferred, however, that the benzene or its chlorine derivative is maintained to be completely dissolved in the organic electrolyte. Further, as the benzene or its chlorine derivative is added, the dielectric constant of the organic electrolyte decreases. Accordingly, the

5 the amount is preferably from 0.1 to 30 wt%, particularly preferably from 1 to 10 wt%, in the electrolyte.

10 electrolyte has high affinity to a pseudo-graphite
surface present on the inner walls of pores of the
carbonaceous material and is likely to be adsorbed in
substitution with the water remaining in fine pores
without being removed by the heat treatment. Thus, the
15 remaining water can readily be expelled from the fine
pores and discharged in the electrolyte outside the fine
pores. When a voltage is applied to the element
impregnated with the electrolyte, such water will readily
be electrolyzed and gasified.

20 The storage of electric charge by formation of an
electric double layer takes place mainly in the interior
of pores. With a conventional electric double layer
capacitor containing no benzene or chlorine derivative in
the electrolyte, if a voltage is applied to the element
25 impregnated with the electrolyte, a gas generated by the
electrolysis of water remaining in the fine pores will

remain in the fine pores, whereby the performance of the electric double layer capacitor tends to deteriorate.

Whereas, in the present invention, as mentioned above, it is considered that the gas generated by the electrolysis
5 by the remaining water by the application of a voltage, will be present outside the fine pores i.e. not in the fine pores. Namely, it is present in macro pores within the activated carbon particles or in spaces among the particles, or it will be discharged as bobbles out of the
10 element. Thus, it is considered that deterioration of the performance of the electric double layer capacitor can be controlled to be little.

However, the decomposition gas generated by the application of a voltage to the element increases the
15 inner pressure of the electric double layer capacitor cell. Accordingly, it is preferred that the application of the voltage during the production process is carried out in a dry atmosphere in an open condition to discharge the generated gas out of the capacitor cell. Here, the
20 open condition is a condition where the element is not accommodated in a cell or even if it is accommodated in a cell, the cell is not closed.

Here, the dry atmosphere preferably has a dew point of not higher than -20°C, more preferably not higher than
25 -30°C, most preferably not higher than -40°C.

The voltage to be applied to the element is

preferably at least 2 V which is higher than the decomposition voltage of water, more preferably at least 2.5 V. The temperature for the application of the voltage to the element is preferably from 15 to 85°C, 5 more preferably from 20 to 70°C. If the voltage is applied under heating, the effect for increasing the durability of the electric double layer capacitor will be large, and the time for application of the voltage can be shortened. However, if the temperature is too high, the 10 initial capacitance tends to decrease, and the internal resistance tends to increase.

Further, in the present invention, it is preferred to maintain the element under reduced pressure after the application of the voltage to the element, whereby the 15 generated gas can more effectively be removed from the element. Here, the "reduced pressure" is preferably a reduced pressure of at most 160 Torr, more preferably at most 10 Torr.

The application of a voltage to the element 20 impregnated with the electrolyte is carried out usually by connecting the electrode constituting a positive electrode for the electric double layer capacitor (hereinafter referred to as the positive electrode of the element) to a plus terminal of a DC power source and 25 connecting the electrode constituting a negative electrode of the electric double layer capacitor

(hereinafter referred to as the negative electrode of the element) to a minus terminal of a DC power source.

However, in order to further increase the durability of the electric double layer capacitor, it is preferred that this application of a voltage is repeated at least once reversing the connection of the positive electrode and the negative electrode. Namely, the application of a voltage to the element preferably comprises the following steps A and B:

10 Step A: a step of applying a voltage across the positive and negative electrodes by a DC power source, and

 Step B: a step of applying a voltage by inversely connecting the positive and negative electrodes to the DC
15 power source as compared with step A.

 Here, either step A or step B may be carried out first, or step A and step B may be repeated alternately.

 With respect to the electrodes in the present invention, both the positive electrode and the negative
20 electrode contain a carbonaceous material having a specific surface area of from 100 to 3000 m²/g for forming an electric double layer at the interface with the electrolyte. As such a carbonaceous material, resin type activated carbon such as phenol, coconut shell type
25 activated carbon, coke type activated carbon, pitch type activated carbon, carbon nanotube, carbon aerogel, carbon

black or polyacene may, for example, be preferably used. The electrodes are preferably formed by adding an organic binder to at least one type of these carbonaceous materials. Particularly, they are preferably formed by
5 adding an organic binder such as polytetrafluoroethylene or polyvinylidene fluoride to a carbonaceous material, followed by molding into a sheet, which is then bonded to a current collector, or by coating a liquid containing a carbonaceous material and the organic binder on a current
10 collector.

In the present invention, the elute contained in the organic electrolyte to store electric charge by forming an electric double layer, is preferably a quaternary onium salt from the viewpoint of the electrical
15 conductivity, the solubility and the electrochemical stability. Particularly, it preferably has a cation represented on $R^1R^2R^3R^4N^+$ or $R^1R^2R^3R^4P^+$, wherein each of R^1 , R^2 , R^3 and R^4 which are independent of one another, is a C_{1-6} alkyl group or a C_{6-10} aryl group. Particularly
20 preferred is a salt comprising such a cation and an anion of e.g. BF_4^- , PF_6^- , $CF_3SO_3^-$, ASF_6^- , $N(SO_2CF_3)_2^-$ or ClO_4^- .

The concentration of the above onium salt in the electrolyte is preferably at least 0.5 mol/l, more preferably at least 1.0 mol/l, for the purpose of
25 securing the ion amount required for forming an electric double layer and for obtaining sufficient electrical

conductivity.

The organic solvent to be used for the organic electrolyte is preferably at least one solvent selected from the group consisting of a cyclic carbonate such as ethylene carbonate, propylene carbonate or butylene carbonate, a linear carbonate such as dimethyl carbonate, ethyl methyl carbonate or diethyl carbonate, sulfolane, a sulfolane derivative and a nitrile such as acetonitrile or glutaronitrile.

10 The separator in the present invention is not particularly limited, but is preferably made of a porous material which is excellent in the electrical insulating property and in the chemical stability against the electrolyte and which is capable of absorbing a large
15 amount of the electrolyte and excellent in the liquid-holding property. Specifically, it is preferably made of inorganic fibers such as glass fibers, silica fibers, alumina fibers or whiskers thereof, natural fibers such as manila hemp, or organic fibers such as synthetic
20 fibers of e.g. polyolefin or polyester. It is preferably a sheet prepared from such fibers. Also preferred is a micro porous film having fine perforations formed by stretching a film made of e.g. polyolefin or polyester.

The structure of electric double layer capacitor of
25 the present invention is not particularly limited and may preferably be any one of a coin structure wherein disk-

shaped positive and negative electrodes face each other
with a separator interposed therebetween and are
impregnated with an electrolyte, a laminated structure
wherein rectangular positive and negative electrodes are
5 alternately laminated with a separator interposed
therebetween, impregnated with an electrolyte and
accommodated in an angular casing, and a winding
structure wherein a pair of strip-shaped positive and
negative electrodes are wound to face each other with a
10 separator interposed therebetween, impregnated with an
electrolyte and accommodated in a cylindrical casing.

Now, the present invention will be described in
further detail with reference to Examples (Examples 1 to
12, 15 and 16) and Comparative Examples (Examples 13 and
15 14). However, it should be understood that the present
invention is by no means restricted by such specific
Examples.

EXAMPLES 1 to 14

80 parts by weight of high purity phenol resin type
20 activated carbon having a specific surface area of 1800
m²/g and an average particle size of 10 μ m, 10 parts by
weight of carbon black as a conductive material and 10
parts by weight of polyethylene tetrafluoroethylene
powder as a binder, were mixed, then kneaded while
25 dropwise adding ethanol and rolled, followed by drying at
200°C for 30 minutes to remove ethanol thereby to obtain

an electrode sheet having a thickness of 140 μm .

The above electrode sheet was bonded to each side of an aluminum foil current collector with a thickness of 40 μm having a lead terminal at a portion having a width of 6 cm and a length of 13 cm, by means of a conductive adhesive, followed by roll pressing to obtain an electrode assembly having the electrode and the current collector integrated and having a thickness of 330 μm , and this assembly was used for positive and negative electrode assemblies.

A sheet made of glass fibers was punched out in a rectangular shape having a width of 6.6 cm and a length of 13.6 cm to obtain a separator. 18 sheets of the above positive electrode assembly and 18 sheets of the above negative electrode assembly were alternately laminated with the separator interposed to obtain an element. This element was vacuum-dried at 200°C for 24 hours and then accommodated in a bottomed angular aluminum metal casing having a height of 15 cm, a width of 7 cm and a thickness of 2.2 cm.

As organic electrolytes, those having the additives identified in Table 1 incorporated in the proportions (the concentrations in the electrolytes) as shown in Table 1 to propylene carbonate solutions having 1.5 mol/l of $(\text{C}_2\text{H}_5)_3(\text{CH}_3)\text{NBF}_4$ dissolved therein, were prepared. Each organic electrolyte was contacted with a molecular sieve

which was preliminarily heated and dehydrated, to remove the water in the electrolyte to a level of not higher than 10 ppm, and then it was injected in the metal casing to impregnate the element therewith.

5 Further, each element was subjected to voltage application treatment in an open condition and reduced pressure treatment, as shown in Table 1. As shown in Table 1, there are some cases wherein neither the voltage application treatment nor the reduced pressure treatment
10 was carried out. In the voltage application treatment, the positive electrode of the element was connected to a plus terminal of a DC power source and the negative electrode of the element was connected to a minus terminal of the DC power source, and a voltage of 2.8 V
15 was continuously applied for 12 hours in a dry atmosphere (dew point: -50°C) while the metal casing was open without sealing. The reduced pressure treatment was carried out after the voltage application treatment by maintaining the element under a reduced pressure of 5
20 torr for one minute.

Then, electrode leads of the positive and negative electrodes were respectively bundled and welded by ultrasonic welding to positive and negative terminals air-tightly and insulatedly attached to an aluminum
25 cover. Then, the cover was fit in the opening of the above metal casing, and the periphery was welded by laser

for sealing to obtain an electric double layer capacitor. With respect to samples of Examples 1, 6 and 13 to which no voltage application treatment in an open condition was applied, after sealing each metal casing, the positive
5 electrode of the electric double layer capacitor was connected to a plus terminal of a DC power source, and the negative electrode was connected to a minus terminal of the DC power source, and a voltage of 2.8 V was continuously applied for 12 hours, whereupon the
10 capacitor was used as a complete sample of the electric double layer capacitor.

The initial service capacitance and the internal resistance of each electric double layer capacitor thus obtained, were measured, and then as an accelerated test
15 on reliability of the performance, this capacitor was maintained in a constant temperature tank of 45°C for 2000 hours while applying a voltage of 2.7 V to carry out a durability test. The service capacitance and the internal resistance after the durability test were
20 measured, and the change in the capacitance and the change in the resistance after the durability test were calculated against the initial properties. The results are shown in Table 2.

EXAMPLE 15

25 An electric double layer capacitor was prepared in the same manner as in Example 3 except that the voltage

application treatment was changed as follows. Namely,
the positive electrode of the element was connected to a
minus terminal of a DC power source and the negative
electrode of the element was connected to a plus terminal
5 of the DC power source, and a voltage of 2.8 v was
continuously applied for 6 hours, in a dry atmosphere
(dew point: -50°C) while the metal casing was open
without sealing. Then, the positive electrode of the
element was connected to the plus terminal of the DC
10 power source, and the negative electrode was connected to
the minus terminal of the DC power source, and a voltage
of 2.8 V was continuously applied for further 6 hours.
The obtained electric double layer capacitor was
evaluated in the same manner as in Example 1. The
15 results are shown in Table 2.

EXAMPLE 16

An electric double layer capacitor was prepared in
the same manner as in Example 15 except that instead of
benzene, 5 wt% of o-dichlorobenzene was incorporated in
20 the electrolyte. This electric double layer capacitor
was evaluated in the same manner as in Example 1. The
results are shown in Table 2.

Table 1

	Additive	Amount (wt%)	Voltage application treatment in an open condition	Reduced pressure treatment
Ex. 1	Benzene	5	Not carried out	Not carried out
Ex. 2	Benzene	5	Carried out	Not carried out
Ex. 3	Benzene	5	Carried out	Carried out
Ex. 4	Benzene	2	Carried out	Carried out
Ex. 5	Benzene	10	Carried out	Carried out
Ex. 6	Monochlorobenzene	5	Not carried out	Not carried out
Ex. 7	Monochlorobenzene	5	Carried out	Not carried out
Ex. 8	Monochlorobenzene	5	Carried out	Carried out
Ex. 9	o-dichlorobenzene	5	Carried out	Carried out
Ex.10	m-dichlorobenzene	5	Carried out	Carried out
Ex.11	p-dichlorobenzene	5	Carried out	Carried out
Ex.12	1,2,4- trichlorobenzene	5	Carried out	Carried out
Ex.13	-	-	Not carried out	Not carried out
Ex.14	Naphthalene	5	Carried out	Carried out

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Sub C.

	Initial stage		After the durability test			
	Service capacitan- ce	Internal resist- ance	Service capacitan- ce	Change in capacitan- ce	Internal resist- ance	Change in capacitan- ce
	(F)	(mΩ)	(F)	(%)	(mΩ)	(%)
Ex. 1	1720	2.8	1430	-17	5.0	+80
Ex. 2	1700	2.7	1450	-15	4.5	+65
Ex. 3	1710	2.7	1470	-14	4.3	+60
Ex. 4	1720	2.9	1440	-15	4.7	+62
Ex. 5	1710	3.0	1400	-16	5.5	+62
Ex. 6	1730	2.5	1440	-17	4.8	+79
Ex. 7	1710	2.6	1440	-16	4.3	+66
Ex. 8	1710	2.6	1470	-14	4.2	+62
Ex. 9	1710	2.8	1500	-12	4.4	+58
Ex.10	1720	2.8	1480	-14	4.5	+61
Ex.11	1710	2.7	1490	-19	4.3	+59
Ex.12	1700	2.7	1280	-19	5.5	+105
Ex.13	1730	3.0	950	-45	8.8	+192
Ex.14	1720	2.9	480	-72	18.9	+520
Ex.15	1710	2.8	1520	-11	4.3	+55
Ex.16	1720	2.7	1530	-11	4.2	+54

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